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Sept. 19, 2004  
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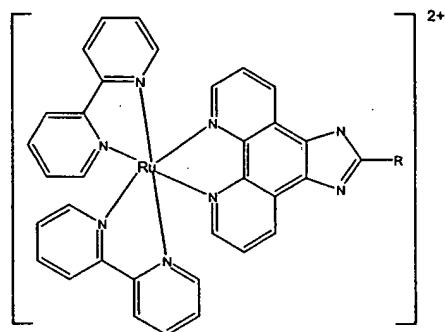
# Ruthenium (II) Polypyridine Complexes for Two-Stage pH Sensing and Its Preparation

(Translated from the Chinese Version)

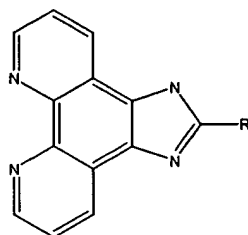
## Abstract

## Claims

1. The ruthenium (II) polypyridine complexes with general chemical structure indicated below:



2. Preparation of ruthenium (II) polypyridine complexes: A mixture of bis (2, 2'-bipyridine) dichlororuthenium (II) bishydrate and a phenanthroline-imidazole derivative ligand with molar ratio 1 : 1 in ethyl alcohol-water (2:1 ~ 5:1, v/v) was refluxed for 5 hrs. The solvent was removed. The product was purified through silica gel column separation with 1:1 ~ 4:1 acetone/toluene as eluent. The general chemical structure of the phenanthroline-imidazole derivatives described here are shown below:



3. As indicated in 2, the solvent used in the preparation is the mixture of ethyl alcohol and water with volume ratio 3:1.
4. Also as indicated in 2, the preparation employs a column separation process, which can be silica gel or  $\text{Al}_2\text{O}_3$  column separation with the mixture of acetone and toluene (2:1, v/v) as eluents.

## Description

### Ruthenium (II) Polypyridine Complexes for Two-Stage pH Sensing and Their Preparation

This patent is on pH photosensors. It is about the preparation of ruthenium (II) polypyridine complexes and their two-stage pH photo-sensing property at both high pH and low pH.

Molecules can probe a substance or some properties of a substance are called molecular sensors. Usually, a molecular sensor consists of a sensing part and a signaling part. The former has the capacity to combine with a specific substance or a target in the mixture while the later can signal this combination. Aroused by the complex natural phenomena, chemists have synthesized a series of complicated molecules as sensors, like crown ethers, cryptands, spherands and calixarenes. These molecules can selectively chelate ions or molecules, which is the base of the molecular sensing. However, the changes of the physical properties due to the combination of crown ethers or the related guests with the target ions or molecules are usually too small to be useful for the practical application. Therefore, a new generation of sensors based on photoactive metal cations was developed. They are called photoactive inorganic cations sensors and composed of three parts: (1) ion-sensing part; (2) photon emitting part and (3) the chemical bridging part of (1) and (2).

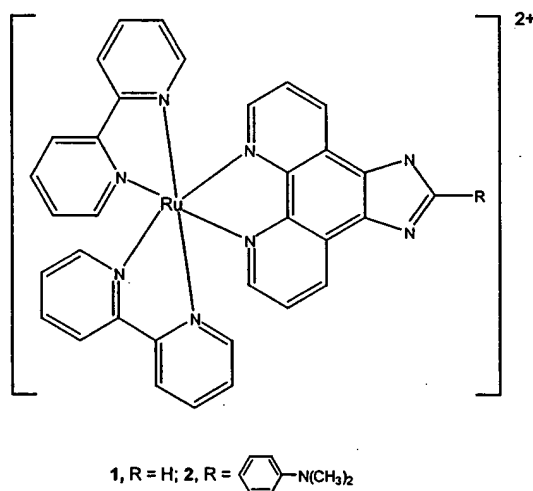
Most of the photoactive sensors are based on the measurement of absorption, emission or refraction, of which emission measurement is most sensitive. The emission wavelength is always longer than the excitation wavelength, which makes it possible to read even very weak emission signals. With the long lifetime, high emission quantum yield, photoactive transition metal complexes sensors usually work much better than typical nanosecond-luminescent sensors. Although a lot of photoactive transition metal complexes have been reported, only ruthenium (II) polypyridine complexes and tricarbonyl( $\alpha$ -bisimino)rhodium(II) complexes have been used as photosensors due to their good thermostability, chemical stability and solubility in water, intense absorption for visible light, high emission efficiency and long luminescent lifetime. Meanwhile, because the excitation states of the complexes are polar, the quantum yield, lifetime as well as redox potential of the excitation states will change with the changes of the surroundings, such as auxiliary ligands, polarity of the solvents.

Almost all of the living processes carry out at certain pH values or pH ranges. For example, there is an apparent difference between the pH inside normal and tumor cells. Thus, a quick and accurate determination of the cell pH is of very importance. Molecules, whose ground state absorption change with pH, have been used for pH monitor for years. But their sensitivity is low due to the low sensitivity of the absorption and they cannot be used for clinic diagnosis. However, pH sensors made from the molecules whose emission spectra depending on pH can be highly sensitive, which are very promising for pH diagnosing applications. So far, research on pH photosensors is still at its early stage and very few reports have been published. The first research on rhodium-bipyridine pH

sensors was done by Grigg in 1992 (*Chem. Comm.* **1992**, 1300.). They attached amines, as the pH sensing parts, to the rhodium bipyridine complex through methylene groups. The protonation and the deprotonation of the amines result in the emission change of the complexes, which monitor the pH change of the solutions. In 1994, Grigg reported a series more complicated pH photosensors, where they used calixarenes as the pH sensing parts and rhodium bipyridine complexes as photon emitting part. Although the emissions of these molecules are very pH-sensitive, their synthesis is a hard work and they are one-stage pH sensors, i.e. they only work in one pH range, either at pH 1-6 or at 7-11.

The goal of this patent was set to overcome the limitation of Grigg's sensors: the sensors are ruthenium bipyridine complexes with simple structures; the nitrogen-containing electron donor binds ruthenium with covalent bonds; the pH-relied emission is realized through the intramolecular ligand-to-metal electron transfer; the two-stage pH sensing is realized through the protonation and deprotonation of the nitrogen-containing donor, which can monitor the pH change at both low pH range and high pH range; the ligands are easy to synthesize with high yield (70~80%).

The general chemical structure of the ruthenium (II) complexes is shown bellow:



**Figure 1.** Structures of 1 and 2

#### Preparation of the ruthenium (II) complexes:

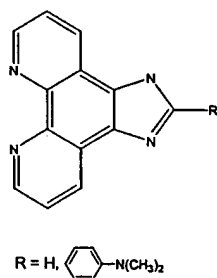
A mixture of  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  and the phenanthroline-imidazole derivative ligand with molar ratio 1 : 1 in ethyl alcohol-water (1:1, v/v) was refluxed for 5 hrs. The mixture was cooled down and filtrated. The solvent in the filtrate was then removed and saturated sodium perchlorate solution was added. The precipitate thus obtained was purified by a silica gel column separation with 1:1 ~ 4:1 acetone/toluene as eluent and then by a recrystallization in ethyl alcohol-water (2:1 ~ 5:1, v/v).

#### Preparation of $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ :

A mixture of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  with 2, 2'-bipyridine with molar ratio 1:1 in DMF was refluxed for 3 hours. The mixture was then concentrated and dark pink crystals were collected by filtration.

#### Preparation of phenanthrolineimidazole ligands:

1, 10-phenanthroline-5, 6-dione was mixed with 4-aminobenzodehyde derivatives and ammonium acetate in molar ratio 1:1:2.5 in glacial acetic acid. The mixture was refluxed for 1 hour. It was cooled down and neutralized with concentrated ammonium hydroxide. The yellow solid was thus obtained. Pure phenanthrolineimidazole ligands were obtainable by a further recrystallization of the solid in methanol. The general chemical structure of the phenanthrolineimidazole ligands is shown in Figure 2.



**Figure 2.** Structure of phenanthrolineimidazole derivatives

The ruthenium polypyridine complexes described here have strong absorption for visible light and emit intensively. The emission intensity of the complexes decreases with the increase of pH. When the pH is increased, the protonated ligands lose the proton first and then the  $-\text{NH}$  of the imidazole group lose its proton, which corresponds to a two-stage pH sensing process. This is why the complexes described here were characterized as two-stage sensors.

## Examples

### Example 1

#### Synthesis of Ruthenium (II) polypyridine complex 1 :

A mixture of 0.2 mmol  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  and 0.2 mmol phenathrolineimidazole ligand (Figure 2,  $\text{R} = \text{H}$ ) in 20 ml ethyl alcohol-water (3:1, v/v) was refluxed for 5 hours and the color turned red-brown. The mixture was cooled down and filtrated. The filtrate was evaporated and purified through a silica gel column separation with acetone/toluene (2:1, v/v) as eluent. The yield was 75%.

#### Characterization of complex 1:

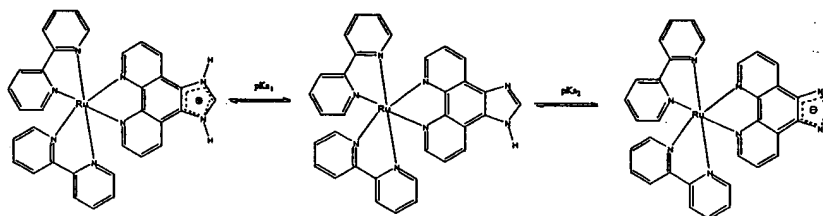
UV absorption:  $\lambda_{\text{max}}(\text{CH}_3\text{CN}) = 453.5 \text{ nm}$ ,  $\epsilon = 1.661 \times 10^4$

$^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ): 8.98 – 8.95 (dd, 2H), 8.57 – 8.50 (q, 4H), 8.41 (s, 1H), 8.07 (ddd, 2H), 7.99 – 7.96 (m, 4H), 7.84 – 7.82 (dd, 2H), 7.74 – 7.72 (q, 2H), 7.55 – 7.54 (m, 2H), 7.42 (m, 2H), 7.18 (m, 2H).

Elemental analysis calcd(%) for  $\text{Ru}(\text{C}_{33}\text{H}_{24}\text{N}_8) \cdot 2\text{ClO}_4 \cdot 3\text{H}_2\text{O}$ : C, 44.71; H, 3.41; N, 12.64; Found: C, 45.24; H, 3.52; N, 12.93%.

The maximum absorptions and emissions as well as the quantum yields of complex 1 at different pH are shown in Table 1. The pKa constants of it are shown in Table 2.

Complex 1 is a base and an acid at the same time. The equilibrium in solution can be expressed as :



When the pH is low, the emission is from the protonated form. When the pH is high, the emission is from the deprotonated form. Therefore two independent changes can be observed at pH 0.35 ~13 for complex 1.



## Example 2

### Synthesis of Ruthenium (II) polypyridine complex **2** :

The preparation procedure is same as complex **1** with a different phenanthrolineimidazole ligand (Figure 2. R = -*p*-C<sub>6</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>2</sub>). The yield for **2** is 58%.

### Characterization of complex **2**:

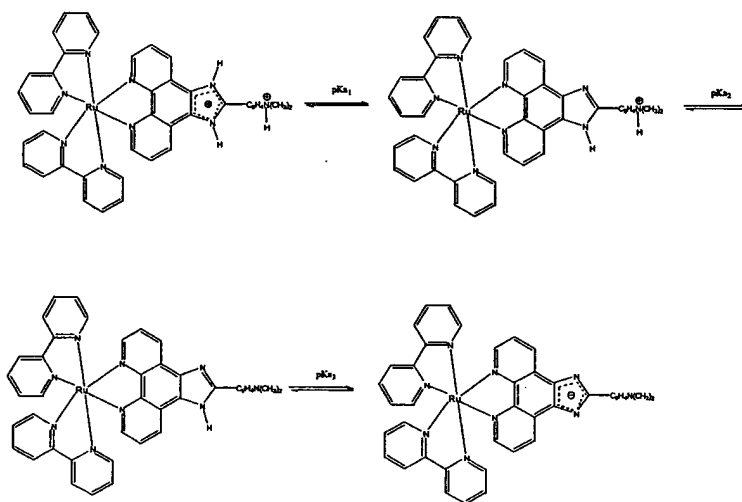
UV absorption:  $\lambda_{\text{max}}(\text{CH}_3\text{CN}) = 457.5 \text{ nm}$ ,  $\epsilon = 2.4 \times 10^4$

<sup>1</sup>H NMR (CD<sub>3</sub>CN): 8.88 (dd, 2H), 8.57 – 8.51 (t, 4H), 8.07 (t, 2H), 7.94 – 7.83 (m, 8H), 7.64 – 7.59 (m, 4H), 7.43 (t, 2H), 7.23 (t, 2H), 6.70 – 6.67 (d, 2H), 2.96 (s, 6H).

Elemental analysis calcd(%) for Ru(C<sub>41</sub>H<sub>33</sub>N<sub>9</sub>) · 2ClO<sub>4</sub> · 2H<sub>2</sub>O: C, 49.86; H, 3.78; N, 12.76; Found: C, 50.12; H, 3.85; N, 12.23%.

The maximum absorptions, maximum emissions and the quantum yields of complex **1** at different pH are shown in Table 1. The pK<sub>a</sub> constants of it are shown in Table 2.

Like complex **1**, complex **2** can also act as a base and an acid. The equilibrium in solution can be expressed as follows:



When pH < 1, the nitrogen atoms on imidazole group and amine group are all protonized. As the increase of the pH, the complex loses the two protons gradually along with the decrease of the emission intensity. Thus, the emission intensity decrease at low pH (pH < 6) is resulted from the electron transfer from the aminobenzene group to Ru (II). When the pH goes higher, the NH on the imidazole group starts to lose its proton. Therefore, the decrease of the emission intensity at higher pH is due to the electron transfer from both the aminobenzene group and the imidazole anion to Ru (II), which makes the sensor even more sensitive at higher pH.

**Table 1.** The maximum absorptions, maximum emissions and the quantum yields of **1** and **2** at different pH.

Complex	<b>1</b>			<b>2</b>		
pH	$\lambda_{em}^{max}(nm)$	$\lambda_{abs}^{max}(nm)$	$\phi(\times 10^3)$	$\lambda_{em}^{max}(nm)$	$\lambda_{abs}^{max}(nm)$	$\phi(\times 10^3)$
1	638	435	34.9	644	436	44.6
3	634	453	39.6	634	358	33.3
7	622	455	41.6	628	460	9.0
12	632	458	26.4	632	462	3.7

**Table 2.** The pKa constants of **1** and **2**

Complex	Absorption Titration <sup>b)</sup>			Emission Titration <sup>a)</sup>		
	pKa <sub>1</sub>	PKa <sub>2</sub>	PKa <sub>3</sub>	pKa <sub>1</sub>	PKa <sub>2</sub>	PKa <sub>3</sub>
1	1.97	10.48 10.46		2.88	10.66	
2	1.97	3.75	10.56		4.22	10.71

<sup>a)</sup> obtained from the MLCT curves; <sup>b)</sup> obtained from the absorption curves

**Bibliographic Information**

**Preparation of ruthenium(II) polypyridine complexes as luminescent pH sensors.** Zhang, Manhua; Jing, Bingwen; Chen, Shen; Shen, Tao; Shen, Jianquan. (Inst. of Chemistry, Chinese Academy of Sciences, Peop. Rep. China). Faming Zhuanli Shenqing Gongkai Shuomingshu (2001), 8 pp. CODEN: CNXXEV CN 1289774 A 20010404 Patent written in Chinese. Application: CN 99-119645 19990924. CAN 137:14840 AN 2002:472861 CAPLUS (Copyright 2002 ACS)

**Patent Family Information**

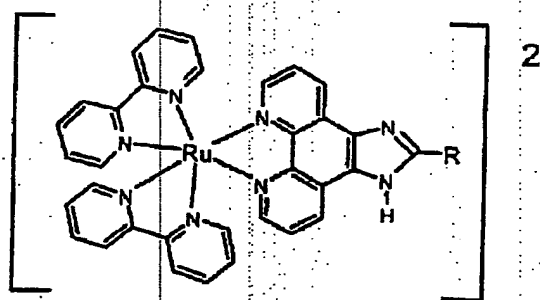
<u>Patent No.</u>	<u>Kind</u>	<u>Date</u>	<u>Application No.</u>	<u>Date</u>
CN 1289774	A	20010404	CN 1999-119645	19990924
CN 1088713	B	20020807		

**Abstract**

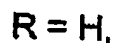
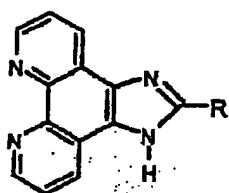
[Ru(bipy)2L](ClO4)2 are prep'd. by mixing [Ru(bpy)2Cl2].2H2O with 2-(R-substituted)-1H-imidazo[4,5-f]-1,10-phenanthroline (L, R = H, 4-Me2C6H4) at a molar ratio of 1:1 in ethanol-water (2-5:1, vol./vol.), refluxing for 5 h, and purifying on silica gel or Al2O3 column with acetone-benzene (1-4:1) as developing agent. The complexes are used for luminescent pH sensors.

## 权 利 要 求 书

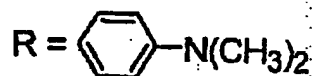
1. 一种钌(II)多吡啶配合物, 其配合离子对应于下列通式:



2. 根据权利要求1所述的一种钌(II)多吡啶配合物的制法, 其特征在于按如下步骤进行: 将二(2,2'-联吡啶)-二氯-二水和钌(II)与菲罗咪咪唑衍生物按摩尔比 1:1 在体积比 2:1~5:1 的乙醇-水中回流 5 小时, 除去溶剂, 进行硅胶柱层析, 用 1:1~4:1 的丙酮/甲苯溶液作淋洗液淋洗, 所述的菲罗咪咪唑衍生物配体的结构为通式:



其中



3. 如权利要求2所述的一种钌(II)多吡啶配合物的制法, 其特征在于所述的溶剂为乙醇与水的混合物, 其体积比例为 3:1.

4. 如权利要求2所述的一种钌(II)多吡啶配合物的制法, 其特征在于所述的层析处理, 可为硅胶或氧化铝层析柱, 其淋洗液为丙酮与甲苯的混合物, 体积比可为 2:1.

## 用于二级 pH 传感的钆(II)多吡啶配合物及其制备方法

本发明属于 pH 发光传感技术领域，特别是属于钆(II)多吡啶配合物制备及其具有在低 pH 值区和高 pH 值区分别响应的二级 pH 发光传感器特性。

传感器或敏感器(sensor)就是对某些性质或分析物发生响应的分子。通常，一个敏感器由一个分子识别组分及一个响应组分组成，前者具有在混合物中与特定物种相结合的能力，后者则能够在结合后立即产生一个与之相应的信号改变。受生物过程中自然复杂现象的启示，化学家们已成功地合成了许多复杂的有机分子，如 王冠醚，穴状配体，球烷，及杯芳烃等，这些分子能与特定的离子或分子螯合，它们是分子识别的基础。一般说来，王冠醚及其相关化合物与特定物种结合后本身不能产生具有识别性的物理性质改变，而这正是信号传输及敏感的基础。为了克服这种困难，新一代的主体分子被用于该领域，其主要是基于过渡金属配合物的发光传感器。这种发光无机离子传感器由三部分组成：(1)一个离子识别位置(2)对分析物发生结合响应的发光组分(3)识别位置及发光组分之间的化学连接。

尽管有许多发光过渡金属配合物，只有钆多吡啶配合物及铈三羧基 $\alpha$ -二亚胺配合物已用于发光探针。这是由于它们的热稳定性、化学稳定性、水溶性、强的可见吸收、有效的发射及长寿命的激发态。而且由于它们的激发态是极性的，其激发态特性如发射量子效率，发射寿命及氧化还原势等在很大程度上会受到辅助配体，溶剂极性，及其他环境因素的影响。在光学传感器中常用的测量方法是吸收、发射或折射光谱，而发射技术具有内在的高灵敏度。由于发射波长总是长于入射波长，这样相对于零或近零背景读出信号是可能的，对于发射的扰动发射信号可以通过强度，强度比或寿命等形式来记录。过渡金属配合物做为发射探针有许多潜在优势，包括长的激发态寿命及高的发射量子产率。与典型的纳秒有机荧光探针相比，长的激发态寿命使得它们很容易测量，而且对无处不在的短寿命的有机发光物质提供了有效的时间区别。

基态吸收随 pH 变化的物质早已用于 pH 的定量测定及 pH 指示剂。但吸收光谱一般是相当不敏感的也难用于远距离光纤及小的 pH 测定。在发射光谱上具有 pH 依赖的发光分子可用作灵敏的 pH 指示剂。相当多的生命现象都是在一定的 pH 条件下进行的，正常细胞和肿瘤细胞中的 pH 有明显的差别。细胞中 pH 值的快速准确测定对于肿瘤诊断也是很有意义的，然而传统的 pH 计是无能为力的。具有灵敏度高、体积小、能远距离测定的发光 pH 传感器在这方面应该具有潜在的应用。尽管这种发光 pH 传感器还处于早期研究阶段，文献报道还不多见，其

前景是很好的。1992 年格里格首次在英国化学会志的化学通讯上(R. Grigg, E. D. J. A. Norgert, J. Chem. Soc. Chem. Commun. 1992, 1300.)报道了基于联吡啶钌配合物的发光 pH 传感器, 它们是联吡啶钌通过亚甲基与各种胺相连, 通过胺的质子化与去质子化来影响配合物的发射而产生 pH 敏感, 配合物的发射性质随 pH 的变化而变化。1994 年格里格又在英国化学会志的化学通讯 (R. Grigg, J. M. Holmes, S. K. Jones, E. D. J. A. Norgert, J. Chem. Soc. Chem. Commun. 1994, 185.)报道了以联吡啶钌为发光单元, 杯芳烃作为酸碱敏感单元的发光 pH 传感器, 研究了这些化合物的发射随 pH 变化的特性。尽管报道的这些分子的发射性质具有 pH 敏感特性, 但化合物的结构复杂, 配体杯芳烃 2, 2'-联吡啶及 5, 5'-二甲基联吡啶不易合成, 且对 pH 只是一级敏感(即只在一个特定 pH 范围内敏感, 如 pH 1-6 或者 pH 7-11)。

本发明的目的在于克服上述缺点, 提供了一种结构简单的钌(II)多吡啶配合物, 其结构特点是将含氮的电子给体共价键与钌配合物相连接, 通过分子内电子转移实现了配合物的发射对 pH 的依赖, 并利用含氮给体的质子化和去质子化实现其发射强度对 pH 在低值和高值区与分别响应, 使其具有二级敏感的特性, 用于高灵敏度二级发光 pH 传感器。且带有酸碱敏感基团的配体通过最容易得到的 5, 6-菲罗啉二酮与醛一步得到, 且产率很高(70%-80%)。

本发明的钌(II)多吡啶配合物, 其配合离子对应于下列通式:

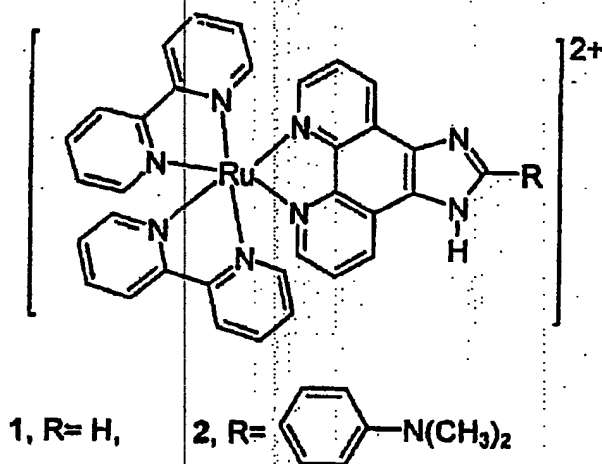


图 1. 化合物 1 及 2 的结构式

本发明的钌多吡啶配合物的制备方法按如下步骤进行:

将  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  与菲罗啉咪唑配体按 1:1 摩尔比与水-乙醇(1:1, v/v)溶剂回流 2 小时, 冷却后过滤, 将滤液除去溶剂, 加入饱和高氯酸钠水溶液, 得沉淀。将此沉淀用柱层

析后经重结晶后得纯净的产物。溶剂为乙醇于水的混合溶剂，其体积比为 2:1~5:1。柱层析可用硅胶或三氧化二铝，淋洗液为丙酮与甲苯的混合物，体积比为 2:1~5:1。

$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  的制法为：将  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  与 2,2'-联吡啶按摩尔比 1:1 于二甲基甲酰胺中回流 3 小时，浓缩后析出紫黑色结晶，过滤即得。菲罗咪咪唑衍生物配体的合成为：将 5,6-菲罗咪二酮与取代的对氨基苯甲醛按 1:1 的摩尔比加入 2.5 当量的醋酸铵在冰醋酸中回流 1 小时后，冷却，用浓氨水中和，此时析出黄色固体，过滤后用甲醇重结晶得到纯的菲罗咪咪唑衍生物配体。

其中菲罗咪咪唑衍生物配体为通式图 2：

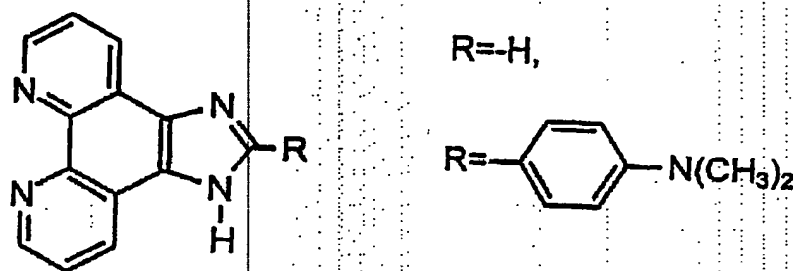


图 2. 菲罗咪咪唑配体的结构式

本发明制备的钌多吡啶配合物在可见光区有强的吸收，在低 pH 的水溶液中有强的发射，随 pH 的增加发射减弱，当 pH 增至含氮电子给体中氮原子去质子时，发射强度急剧减弱，表现出高的 pH 敏感性。在 pH 进一步升高到咪唑二级氮原子上的氢原子电离时，发光强度进一步减弱，这时表现出对 pH 的第二级敏感。因此本发明的配合物可用于二级敏感的发光 pH 传感器。

该发明利用了含氮强电子给体能有效地淬灭钌(II)多吡啶配合物的发射这一特点，设计了将含氮强电子给体共价键与钌配合物相连接的目标化合物，通过分子内电子转移实现了目标化合物的发射对 pH 的依赖，并利用了氮原子的质子化与去质子化及氢原子的电离等性质实现了对 pH 变化具有二级敏感的特性，即在 pH3-6 和 pH9-11 两个区域。目标化合物结构简单，制备易行，分子稳定，发射强且对 pH 变化敏感度高，可用于高灵敏度的二级发光 pH 传感器。

下面结合实施例详述本发明

## 实施例 1

### 钉(II)吡啶配合物 1 的制备方法

0.2mmol  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , 0.2mmol, 0.2mmol 菲罗咪唑配体(结构为图 2 中,  $\text{R}=\text{H}$ ), 20ml 乙醇-水(3:1, v/v)回流 5 小时, 溶液变为棕红色. 冷却后过滤, 蒸去乙醇加入 5ml 水溶解后, 再加入 10ml 饱和高氯酸钠水溶液, 立即析出黄色沉淀, 过滤, 用硅胶柱层析, 丙酮/甲苯(2:1, v/v)淋洗得产物. 产率 75%.

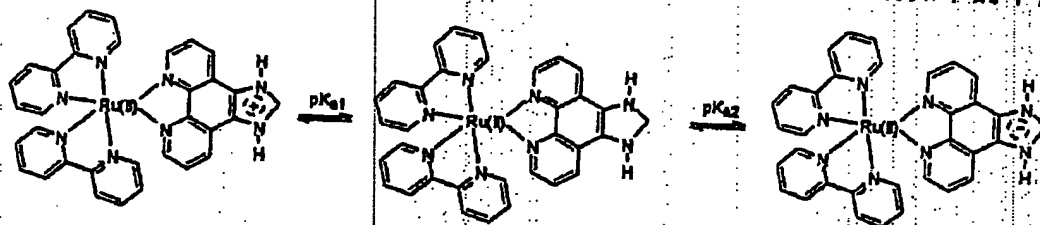
### 此化合物的鉴定

紫外吸收:  $\lambda_{\text{max}}(\text{CH}_3\text{CN})$  453.5nm( $\epsilon=1.661 \times 10^4$ ).

核磁共振:  $^1\text{HMR}(\text{CD}_3\text{CN})$ : 8.98-8.95(dd, 2H), 8.57-8.50(q, 4H), 8.41(s, 1H), 8.07(ddd, 2H), 7.99-7.96(m, 4H), 7.84-7.82(dd, 2H), 7.74-7.72(q, 2H), 7.55-7.54(m, 2H), 7.42(m, 2H), 7.18(m, 2H).

元素分析: 分子式  $\text{Ru}(\text{C}_{33}\text{H}_{24}\text{N}_8) \cdot 2\text{ClO}_4 \cdot 3\text{H}_2\text{O}$ , 理论值 C, 44.71%, H, 3.41%, N, 12.64%, 测量值: C, 45.24%, H, 3.52%, N, 12.93%.

在给定 pH 时, 化合物 1 的吸收波长及发射量子产率于表一, 其  $\text{pK}_a$  值例于表二. 其中含咪唑既是弱酸又是弱碱, 故介质 pH 变化会影响其发射, 化合物 1 有如下的平衡关系:



当 pH 低时, 发射主要来自于质子化的配合物; pH 高时, 发射主要来自去质子的化合物 1, 故在 pH 0.35-13 间发射出现两个明显的突变.

## 实施例 2

钉多吡啶配合物 2( 结构如图 1 中  $\text{R}=\text{—C}_6\text{H}_4\text{—N}(\text{CH}_3)_2$  )

制备方法同化合物 1, 所用菲罗咪唑配体为图 2 中  $\text{R}=\text{—C}_6\text{H}_4\text{—N}(\text{CH}_3)_2$



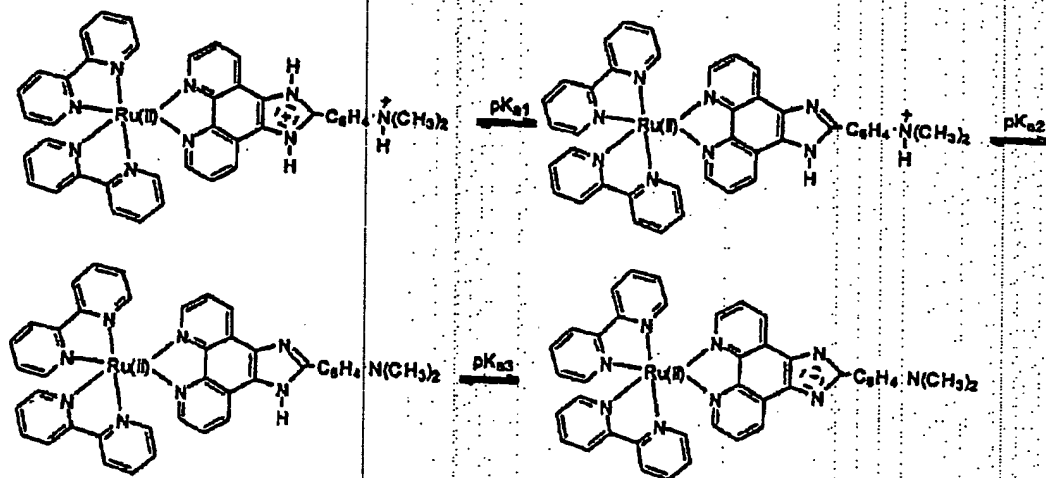
产率, 58%. 此化合物的鉴定:

紫外吸收:  $\lambda_{\text{max}}$  (CH<sub>3</sub>CN) 457.5 nm ( $\epsilon=2.40 \times 10^4$ ).

核磁共振: <sup>1</sup>H NMR (CD<sub>3</sub>CN): 8.88 (dd, 2H), 8.57-8.51 (t, 4H), 8.07 (t, 2H), 7.94-7.83 (m, 8H), 7.64-7.59 (m, 4H), 7.43 (t, 2H), 7.23 (t, 2H), 6.70-6.67 (d, 2H), 2.96 (s, 6H).

元素分析: 分子式 Ru(C<sub>41</sub>H<sub>33</sub>N<sub>9</sub>)·2ClO<sub>4</sub>·2H<sub>2</sub>O, 理论值: C, 49.86%, H, 3.78%, N, 12.76%, 测量值: C, 50.12%, H, 3.85%, N, 12.23%.

在给定 pH 时化合物 2 的吸收波长, 发射波长及发射量子产率列于表 1, 其 pK<sub>a</sub> 值列于表 2. 对于化合物 2, 存在下面的酸碱平衡关系:



当 pH < 1 时, 咪唑及 N,N-二甲基苯胺上的三 N 原子均被质子化, 随着 pH 的增加咪唑和苯胺上的 N 原子相继去质子化, 2 的发射有较大的减弱, 故在低 pH 区域 (pH < 6), 这种发射的减弱来源于苯胺向钌配合物的分子内电子转移, 当 pH 进一步升高到达咪唑上二级 N 上的 H 发生电离, 这时 2 的发射减弱来自于苯胺向配合物的电子转移及负离子本身使配合物的发射减弱, 敏感度大大提高.

表 1. 化合物 1、2 在给定 pH 时的吸收波长、发射波长及发射量子产率

化合物	1			2		
pH	$\lambda_{\text{em}}^{\text{max}}$	$\lambda_{\text{abs}}^{\text{max}}$	$10^3\phi$	$\lambda_{\text{em}}^{\text{max}}$	$\lambda_{\text{abs}}^{\text{max}}$	$10^3\phi$
1	638	435	34.9	644	436	44.6
3	634	453	39.6	634	458	33.3
7	622	455	41.6	628	460	9.0
12	632	458	26.4	632	462	3.7

表 2. 1、 2 的  $pK_a$  值

化合物	吸收滴定			发射滴定		
	$pK_{a1}$	$pK_{a2}$	$pK_{a3}$	$pK_{a1}^*$	$pK_{a2}^*$	$pK_{a3}^*$
1	1.97 <sup>a</sup>	10.48 <sup>a</sup> , 10.46 <sup>b</sup>		2.88	10.66	
2	1.97 <sup>a</sup>	3.75 <sup>b</sup>	10.56 <sup>b</sup>		4.22	10.71

a: 经 MLCT 曲线得到, b: 经紫外的吸收变化得到.

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